

# Photoluminescence excitation measurements on erbium implanted GaN

J. T. Torvik<sup>a)</sup> and R. J. Feuerstein

*Department of E&CE, University of Colorado, Boulder, Colorado 80309-0425*

C. H. Qiu

*Astralux, Inc., 2500 Central Avenue, Boulder, Colorado 80301-2845*

J. I. Pankove<sup>b)</sup>

*Department of E&CE, University of Colorado, Boulder, Colorado 80309-0425*

F. Namavar

*Spire Corporation, 1 Patriots Park, Bedford, Massachusetts 01730-2396*

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The temperature dependence of the optical excitation cross section of Er implanted *n*-type GaN was studied using photoluminescence excitation spectroscopy. Due to the large 3.4 eV band gap of GaN, it was possible to probe two Er absorption lines using a tunable Ti:sapphire laser in the 770–1010 nm range. Photoluminescence excitation spectra exhibiting several Stark splittings revealed a complex dependence upon temperature. The largest excitation cross section in the third excited state was  $1.65 \times 10^{-20} \text{ cm}^2$  at an excitation wavelength of 809.4 nm when measured at 77 K. This value is roughly three times larger than the cross section in the second excited state at  $4.8 \times 10^{-21} \text{ cm}^2$  when pumping at 983.0 nm. The Er-related photoluminescence was reduced between 1.5 and 4.8 times when going from 77 K to room temperature, except when pumping around 998 nm. At this excitation wavelength the room temperature photoluminescence was stronger by a factor of 1.26 compared to that at 77 K. © 1997 American Institute of Physics. [S0021-8979(97)00816-5]

## I. INTRODUCTION

Er-doped semiconductors have been extensively studied during the last decade for potential optoelectronic applications. An electrically pumped, temperature insensitive, broadband and compact optical amplifier or source of 1540 nm light is of great interest for optical fiber communications. Unfortunately, rapid advancement of Er-doped semiconductors has been hampered by fundamental problems such as the characteristic thermal quenching of the  $\text{Er}^{3+}$ -related photoluminescence (PL) intensity.<sup>1</sup> The luminescence is often quenched by several orders of magnitude when going from 77 K to room temperature using semiconductor hosts such as Si and GaAs. The luminescence efficiency at room temperature can be enhanced using impact excitation<sup>2</sup> and codoping with light elements such as O and F.<sup>3</sup> However, the thermal quenching effect is still present, but to a lesser extent.

Wilson *et al.*<sup>4</sup> and our group have previously reported on the temperature dependence of the  $\text{Er}^{3+}$ -related photo-, and cathodoluminescence in *n*-type GaN on sapphire substrates.<sup>5,6</sup> Using direct optical excitation (below band gap excitation), indirect optical excitation (above band gap excitation), and impact excitation, the thermal quenching of the  $\text{Er}^{3+}$ -related luminescence intensity at 1539 nm was found to only be partially explained by a reduction in the luminescence lifetime when going from 77 K to room temperature.

In this article, we report on the optical excitation spectroscopy for Er in GaN at excitation wavelengths ranging from 770 to 1010 nm at room temperature and at 77 K. One advantage with using a wide band gap host such as GaN ( $E_{\text{gap}}=3.4 \text{ eV}$ ), is that the large band gap allows for the

investigation of several absorption lines which are not available using smaller band gap hosts such as Si. The temperature dependence of the  $\text{Er}^{3+}$ -related PL intensity at 1539 nm was found to strongly depend upon the excitation wavelength. At the strongest photoluminescence excitation (PLE) peaks, namely at 809 and 983 nm, the thermal quenching of the PL intensity was as large as a factor of 5 when going from 77 K to room temperature. At other PLE peaks, such as at 822 nm, the PL intensity was reduced much less over the same temperature range. In fact, pumping at 998 nm resulted in a stronger PL intensity at room temperature than at 77 K. However, the PLE peaks are still much weaker when compared to the PLE peaks at 809 and 983 nm.

## II. EXPERIMENT

The GaN layers used in this study were grown by the halogen chemical vapor deposition method on *R*-plane (1102) sapphire substrates, and is described in detail elsewhere.<sup>7</sup> We have previously shown that GaN films grown on *C*-plane (0001) sapphire substrates by metalorganic chemical vapor deposition (MOCVD) are also suitable hosts for Er.<sup>6</sup> The GaN films were *n*-type with carrier concentration  $\sim 10^{18} \text{ cm}^{-3}$ , and a Hall mobility of  $\sim 150 \text{ cm}^2/\text{V s}$ . The GaN films were implanted with  $[\text{Er}^{2+}]=2 \times 10^{15} \text{ ions/cm}^2$  at 350 keV, and coimplanted with  $[\text{O}^+]=10^{16} \text{ ions/cm}^2$  at 80 keV. The energy of the coimplanted O was chosen to make the O and Er implantation spatially overlap. The implantation damage caused by the bombardment of Er ( $Z=68$ ) ions, was partially repaired by high temperature anneals performed at 800 °C for 45 min in flowing  $\text{NH}_3$ . The anneals took place at atmospheric pressure in the quartz reactor of a MOCVD system. The  $\text{NH}_3$  was used to prevent the GaN from decomposing at elevated tem-

<sup>a)</sup>Electronic mail: torvik@spot.colorado.edu

<sup>b)</sup>Also with: Astralux, Inc., 2500 Central Ave., Boulder, CO 80301.

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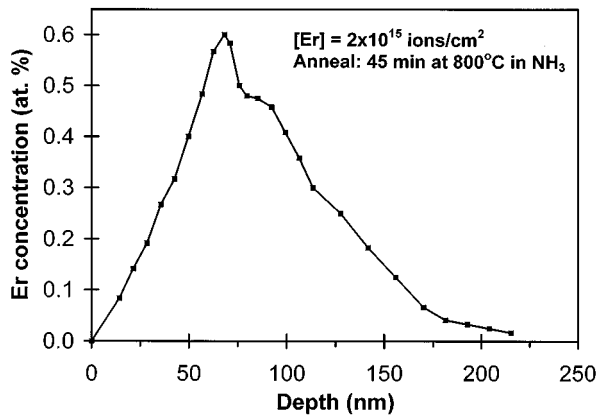


FIG. 1. Er concentration profile in GaN as determined by Rutherford backscattering spectroscopy. The GaN:Er,O sample was implanted with  $[\text{Er}^{2+}] = 2 \times 10^{15}$  ions/cm<sup>2</sup> at 350 keV.

peratures. A detailed description of the GaN:Er,O sample preparation conditions has been reported elsewhere.<sup>8</sup>

PLE spectroscopy experiments were conducted using a tunable Ti:sapphire laser from 770 to 1010 nm. The laser spot size was  $\sim 1$ –2 mm in diameter, and a typical power level was 250 mW. PLE measurements were performed at room temperature and at 77 K using a liquid nitrogen cooled cryostat. The emitted light was collected by a lens (numerical aperture = 0.5) through a 32 cm single-pass grating (blazed at 1500 nm) monochromator, and detected using a thermoelectrically cooled InGaAs photodiode. A bandpass filter (1500–1650 nm) was used in front of the detector. The PL signals were measured with a lock-in amplifier and recorded using a computer. The luminescence data shown are not corrected for the spectral responses of the bandpass filter, detector, or the spectrometer grating, although the corrections are less than 20% over the wavelength range of interest (1500–1650 nm).

### III. RESULTS AND DISCUSSION

#### A. Er doping profiles

The Er concentration profile in *n*-type GaN was measured using Rutherford backscattering spectroscopy with 1.7 MeV He<sup>+</sup> ions. A buried Er profile with full width half maximum (FWHM) of  $\sim 80$  nm, and a peak depth of about 70 nm was found as shown in Fig. 1. Most of the Er was located within 200 nm of the sample surface. The peak Er concentration was  $\sim 0.6$  at. % in a sample implanted with  $[\text{Er}] = 2 \times 10^{15}$  ions/cm<sup>2</sup>.

#### B. Photoluminescence excitation spectroscopy

A typical PLE spectrum as measured on a GaN:Er,O sample at 77 K is shown in Fig. 2. The excitation wavelength was tuned from 785 to 1010 nm with constant power of 250 mW. The spectral resolution was about 0.5 nm. The signal was monitored at the strongest Er<sup>3+</sup>-related emission peak located at 1539 nm. Two typical PL spectra, measured at 77 K and at room temperature, of the same GaN:Er,O sample excited with 250 mW at 809 nm are shown in Fig. 2(a).

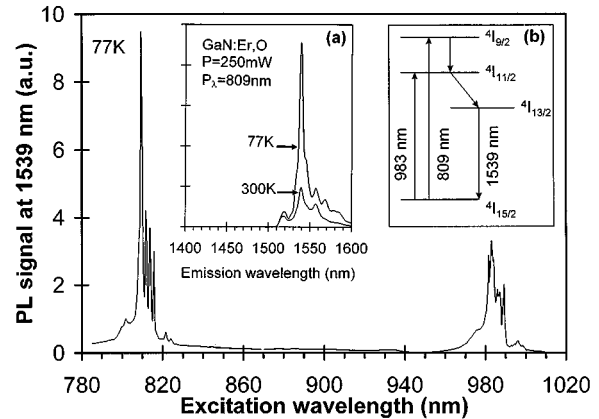


FIG. 2. Photoluminescence excitation spectrum of a GaN:Er,O sample measured at 77 K. The Er<sup>3+</sup>-related photoluminescence signal at 1539 nm was used as a monitor. The spectral resolution was about 0.5 nm. Two typical photoluminescence spectra measured at room temperature and at 77 K are shown by inset (a). Inset (b) is a schematic of the Er<sup>3+</sup> energy levels involved in the absorption and emission processes.

Figure 2(b) is a schematic of the Er<sup>3+</sup> energy levels involved in this PL process. The pumping around 809 nm excites the Er<sup>3+</sup> ions to the third excited  $^4I_{9/2}$  state, labeled with the standard Russell–Saunders (L–S coupling) notation. From the  $^4I_{9/2}$  state the Er ions quickly relax nonradiatively to the first excited  $^4I_{13/2}$  state. The characteristic Er<sup>3+</sup>-related 1539 nm PL corresponds to a radiative transition from the first excited state and to the  $^4I_{15/2}$  ground state. No PL signal was detected between 900 and 1010 nm with a detection sensitivity 1000 times greater than that used for the 1539 nm signal. The  $^4I_{11/2}$ – $^4I_{15/2}$  (980 nm) transition was previously observed in the electroluminescence spectrum from GaN:Er,O.<sup>9</sup>

Seven distinct peaks are present in both the excitation manifolds ( $^4I_{9/2}$  and  $^4I_{11/2}$ ) in the PLE spectrum shown in Fig. 2. The individual peaks are probably Stark splitting's signatures, which are caused by the crystal field. The strongest PLE peak is located at 809.4 nm, and the second strongest peak at 811.7 nm. The energy separation between these peaks is  $\sim 4.2$  meV. At 77 K the 4*f* electrons can gain enough thermal energy ( $\sim 6.7$  meV) to be excited among the Stark splittings. Therefore, it is difficult to estimate with any certainty the lattice location of the Er ions using the number of absorption and emission peaks observed in the PLE and PL spectra. To be conclusive about the lattice location, ad-

TABLE I. Er<sup>3+</sup> excitation peaks.

Peak	$^4I_{15/2} \rightarrow ^4I_{11/2}$		$^4I_{15/2} \rightarrow ^4I_{9/2}$	
	GaN (nm)	LaF <sub>3</sub> (nm) <sup>a</sup>	GaN (nm)	LaF <sub>3</sub> (nm) <sup>a</sup>
1	981.6	982.4	801.8	801.7
2	983.0	986.0	809.4	806.3
3	984.1	987.4	811.6	808.0
4	986.0	988.8	813.7	813
5	987.1	990.8	815.8	819.6
6	989.3	991.8	821.5	--
7	995.8	--	824.0	--

<sup>a</sup>See Ref. 12.

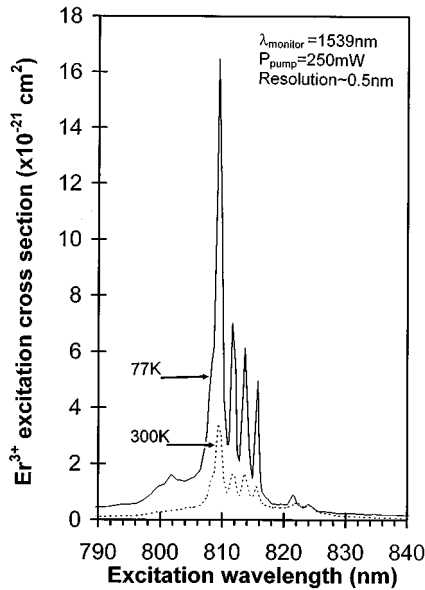


FIG. 3.  $\text{Er}^{3+}$ -related effective excitation cross section ( $\sigma$ ) in GaN measured at 77 K (solid line) and at room temperature (broken line) when pumping to the  $^4I_{9/2}$  manifold.

ditional lower temperature ( $< 10$  K) PLE experiments probing the first excited state ( $^4I_{13/2}$ ) are needed.<sup>10,11</sup> In Table I the peak excitation wavelengths are listed and compared to similar results in  $\text{LaF}_3$ .<sup>12</sup>

### C. Excitation cross section

We have previously shown that the decrease in the  $\text{Er}^{3+}$ -related PL intensity between 77 K and room temperature when pumped at 983 nm cannot be explained by a reduction in luminescence lifetime alone.<sup>5</sup> We decided to investigate the absorption process by tuning the excitation

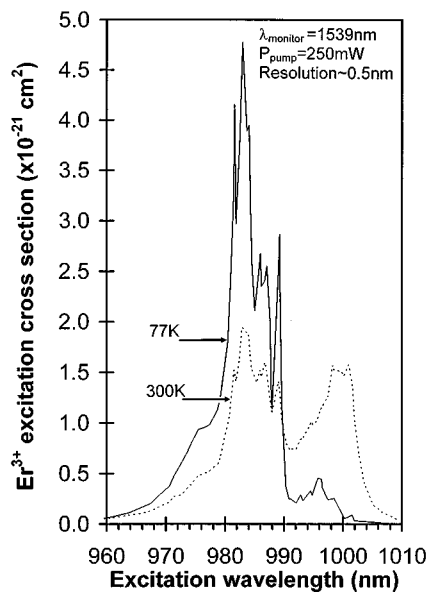


FIG. 4.  $\text{Er}^{3+}$ -related effective excitation cross section ( $\sigma$ ) in GaN measured at 77 K (solid line) and at room temperature (broken line) when pumping to the  $^4I_{11/2}$  manifold.

wavelength at room temperature as well as at 77 K. Two typical PLE spectra from a GaN:Er,O sample measured at 77 K and at room temperature are shown in Figs. 3 and 4. Since the PLE spectrum is a measure of the effectiveness of producing  $\text{Er}^{3+}$ -related luminescence at 1539 nm, the effective excitation cross section of Er in GaN can be calculated using the following expression, assuming small absorption of the pump light (i.e., such that  $P_{\text{PL}}/P_{\text{pump}} \sim \sigma N_{\text{Er}}$ ):

$$\sigma = \frac{P_{\text{PL}}/P_{\text{pump}}}{\eta_r \eta_E \alpha_{\text{PL}} F_{\text{col}} N_{\text{Er}}} \quad (1)$$

where the radiative efficiency ( $\eta_r$ ) is given by  $\tau/\tau_R$ ,  $\tau$  is the observed luminescence lifetime,  $\tau_R$  is the radiative lifetime,  $\eta_E$  is the energy conversion efficiency, and  $\alpha_{\text{PL}}$  is the combined loss in the collection optics, monochromator (slits and optical bandwidth), optical filter, and chopper.  $F_{\text{col}}$  is the fraction of PL power collected in the solid angle of the lens, assuming uniform emission into  $4\pi$  steradians.  $N_{\text{Er}}$  is the Er implantation fluence, and  $P_{\text{PL}}$  is the measured PL power. A radiative lifetime of 10 ms—based on an average of lifetimes measured in a variety of crystals<sup>13</sup>—and a PL lifetime of 2.65 ms were used.<sup>5</sup> The lifetimes were assumed to remain constant with excitation wavelength (770–1020 nm). The index of refraction of GaN was taken to be 2.3 at 1539 nm.<sup>14</sup> The output power from the pump laser was 250 mW over the scanned wavelength range. The break in the PLE spectra around 870 nm indicates a mirror change in the Ti:sapphire laser to span the wavelength region of interest. Since no PL at 980 nm was observed, it was assumed that all the Er ions excited to the  $^4I_{9/2}$  and  $^4I_{11/2}$  states decayed nonradiatively to the  $^4I_{13/2}$  state. The estimate for the optical excitation cross section should be correct to within a factor of 2–4. The uncertainty in  $\sigma$  is due to the uncertainty in the radiative lifetime of Er in GaN ( $\sim 10$  ms), and nonradiative processes such as excited state absorption, cross relaxation, and concentration quenching.<sup>15</sup>

The largest optical excitation cross section for Er in  $n$ -type GaN at 77 K is in the third excited  $^4I_{9/2}$  manifold at 809.4 nm. It is estimated to be  $1.65 \times 10^{-20} \text{ cm}^2$ . This excitation cross section is 3.4 times larger than the strongest excitation peak in the second excited  $^4I_{11/2}$  manifold, which was estimated at  $4.8 \times 10^{-21} \text{ cm}^2$  and located at 983.0 nm. This is an unexpected result since the absorption coefficients in glass show a smaller value for 800 nm than 980 nm.<sup>15</sup> The absorption could be affected by defect levels in the GaN, but Qiu *et al.*<sup>16</sup> did not note any in their photoconductivity study. Another possibility is the presence of nonradiative relaxation, which we have assumed to be zero. In any case it is important to note that this measurement is a combination of absorption and emission cross sections.

The 980 nm results agree with the optical absorption cross section measurements for Er in a variety of glasses ( $1\text{--}3 \times 10^{-21} \text{ cm}^2$ ).<sup>15</sup> The FWHM of the Stark lines in both the  $^4I_{9/2}$  and  $^4I_{11/2}$  manifolds were about 0.5–1 nm. The linewidths were determined by the spectral resolution of the Ti:sapphire laser system. Each of the manifolds are spread over a 50 meV range, which roughly corresponds to the width of the PL in the 1539 nm spectral region.

TABLE II. The fractional change in the peak (1539 nm) and integrated (1500–1600 nm)  $\text{Er}^{3+}$ -related luminescence intensity when going from 77 K to room temperature using four different excitation wavelengths.

	Excitation wavelength			
	809 nm	822 nm	983 nm	998 nm
Peak $\frac{I_{300\text{ K}}}{I_{77\text{ K}}}$	0.21	0.68	0.28	1.26
Integrated $\frac{I_{300\text{ K}}}{I_{77\text{ K}}}$	0.36	0.81	0.43	1.91

It was believed that a shift in the  $\text{Er}^{3+}$ -related excitation peaks might be the reason for the observed  $\text{Er}^{3+}$ -related PL intensity temperature dependence at 1539 nm. However, the location of the PLE peaks remain constant to within 0.5 nm when going from 77 K to room temperature. The temperature quenching is clearly illustrated by PLE spectra shown in Figs. 3 and 4. The reduction in the peak  $\text{Er}^{3+}$ -related PL intensity between 77 K and room temperature is listed in Table II for four different excitation wavelengths.

An interesting feature illustrated in Table II is the fact that the  $\text{Er}^{3+}$ -related peak PL intensity at 1539 nm is actually stronger at room temperature than at 77 K when pumped at 998 nm. To the best of our knowledge, this is the first report of such an effect in a semiconductor host. This effect is more pronounced in the integrated intensity (1500–1600 nm), which is almost twice as strong at room temperature as compared to 77 K. This is due to the fact that the PL spectrum is broadened at room temperature. A similar, but not so dramatic effect takes place when pumping at 822 nm. As mentioned above, it is important to note that the resulting PL intensity is still much less than when pumping at 983 and at 809 nm.

Since the PLE peaks at 809, 822, 983, and 998 nm have a different temperature dependence, it might point towards several different Er centers being optically active. The Er ions could be situated in substitutional or interstitial lattice sites, or two different optically active Er–O complexes could be involved.<sup>5</sup> An alternative explanation is that PLE peaks at 822 and 998 nm are phonon replicas (anti-Stokes process) of the other PLE peaks. The energy of the absorbed phonons are in the 19–25 meV range. This energy is much smaller than both the LO and TO phonons observed in GaN, which are in the 65–92 meV range.<sup>14</sup> The low energy phonons therefore may be local modes from the Er–O complexes. Another possible explanation is the change in the electron distribution with temperature.

## IV. CONCLUSIONS

We have measured the photoluminescence excitation spectrum from 770 to 1010 nm in Er-doped GaN and determined an optical excitation cross section at room temperature and at 77 K. This wavelength range covers the second ( $^4I_{11/2}$ ) and the third ( $^4I_{9/2}$ ) excited states of  $\text{Er}^{3+}$ . The largest cross section in the ( $^4I_{9/2}$ ) manifold at 77 K was  $1.65 \times 10^{-20} \text{ cm}^2$  at 809.4 nm. This value is roughly three times larger than the cross section in the ( $^4I_{11/2}$ ) manifold of  $4.8 \times 10^{-21} \text{ cm}^2$  at 983 nm. This result is surprising given the larger absorption coefficient at 980 nm. Further work is needed to explain this effect.

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